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ANTHRAQUINONYL-TRIAZINES

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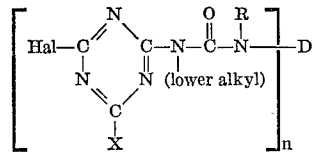
No Drawing. Division of application Ser. No. 800,300, Nov. 8, 1968, which is a continuation of application Ser. No. 517,998, Jan. 3, 1966, which in turn is a continuation-in-part of application Ser. No. 380,677, July 6, 1964. This application May 7, 1970, Ser. No. 35,581

Int. Cl. C07d 55/46

U.S. Cl. 260—249 3 Claims

ABSTRACT OF THE DISCLOSURE

Anthraquinone dyestuffs of the formula



wherein

D is an anthraquinone dyestuff radical;



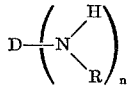
is connected to an aromatic ring carbon of D;
R is H or lower alkyl;
Hal is F, Cl or Br;
n is one of the integers 1 or 2 and
X is a monovalent electron-donor substituent,

selected from the group of lower alkoxy, phenoxy, halogen-substituted phenoxy, lower alkyl-substituted phenoxy, lower alkoxy-substituted phenoxy, lower alkylthio, phenylthio, halogen-substituted phenylthio, lower alkyl-substituted phenylthio, lower alkoxy-substituted phenylthio, lower alkylamino, di(lower)alkylamino, phenylamino, N-lower alkyl-N-phenylamino, N-lower alkyl-N-halogenphenylamino, N-lower alkyl-N-lower alkylphenylamino, N-lower alkyl-N-lower alkoxyphenylamino, piperidino or morpholino, halogen being chloro or bromo.

This application is a divisional application of application Ser. No. 800,300 filed November 8, 1968, which application in turn is a continuation application of application Ser. No. 517,998, filed Jan. 3, 1966, now abandoned which latter application is in turn a continuation-in-part of application Ser. No. 380,677 filed July 6, 1964 now abandoned.

The present invention relates to reactive dyestuffs, processes for the production thereof, their use for the dyeing of organic textile fibers containing hydroxyl and/or amino groups, as well as, as industrial product, the fiber materials dyed with the aid of these dyestuffs.

It has been found that dyestuffs which, surprisingly, can be fixed onto textile fibers containing hydroxyl and amino groups and afford dyeings of good fastness properties, are obtained by reacting one mol of an organic dyestuff of the formula

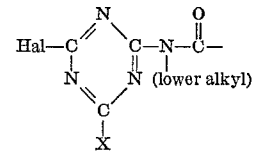


(I)

wherein

D represents the radical of an organic dyestuff capable of withstanding the conventional conditions of dyeing textile fibers containing in their molecule hydroxyl and/or amino groups with fiber-reactive dyestuffs, and subsequent fixation by thermofixing or steaming,
R represents hydrogen or lower alkyl, and
n represents 1 or 2,

with *n* mol of a compound capable of yielding the radical of the formula

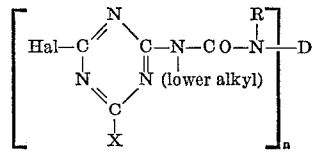


(II)

wherein

Hal represents halogen of one of the atomic numbers 9, 17 or 35, i.e. fluorine, chlorine or bromine, and
X represents a monovalent electron-donating substituent containing a hetero atom of one of the atomic numbers 7, 8 and 16, by way of which atom said substituent is linked to the triazinyl ring in Formula II, and the molecular weight of which substituent does not exceed 200,

to form a dyestuff of the formula



(III)

wherein

D, R and *n* have the same meanings as in Formula I, and Hal and X have the same meanings as in Formula II,

or by forming the reactive dyestuffs of Formula III from components of which at least one contains the radical of Formula II bound by way of an amino group of the formula



"Lower" as used in this specification and in the appended claims in connection with "alkyl," "alkoxy" and the like radicals means that these radicals have from 1 to 5 carbon atoms, unless expressly stated otherwise.

It would have been expected that a triazinyl radical which is attached to a urea bridge, as it is the case in Formula III, would not resist the severe conditions of dyeing textile fibers with fiber-reactive dyestuffs, namely, in particular, strong alkaline dye liquors of pH values in the order of 10 and higher, and treatment, at least during subsequent thermofixation or steaming at elevated temperatures of about 100 to 160° C. in a strongly alkaline medium, but that the triazinyl lower alkylamino radical would be split from the —CO—NR— bridge of Formula III during dyeing, so that no fixation of the dyestuffs to the fiber molecule could take place.

Indeed, this would occur if X in Formula III would represent an electron-accepting substituent. Furthermore, intermediates with such a substituent would not be readily available.

It is one surprising feature of the dyestuffs according to the invention that the bond of the triazinyl radical to the urea bridge in the dyestuffs of Formula III, in which X has the above-defined meaning, and via the urea bridge to the dyestuff-character imparting principal moiety of the molecule in Formula III is so strong that the severe conditions of reactive dyeing, especially on cotton but also on wool or nylon, are withstood without substantial decomposition, and that commercially useful dyeings of satisfactory fastness properties are obtained.

The reaction between the fiber molecule and the reactive dyes falling under Formula III takes place substantially entirely by splitting off the "Hal" substituent from the triazinyl reactive group.

In Formulas I and III, D represents in particular the radical of, for example, a mono-, dis- or poly-azo dyestuff which may contain heavy metal in complex bond, an anthraquinone, a nitro or a phthalocyanine dyestuff.

In those compounds of Formula III in which D represents the radical of an azo dyestuff it is, for example, the radical of a monoazo dyestuff of the benzene-azo-benzene, benzene-azo-naphthalene, benzene-azo-pyrazole, benzene-azo-acetoacetylarylamide, naphthalene-azo-naphthalene and naphthalene-azo-pyrazole series, or the radical of a disazo dyestuff of the benzene-azo-benzene-azo-benzene, benzene-azo-naphthalene-azo-benzene and naphthalene-azo-benzene-azo-benzene series, all of which may be free from or may contain heavy metal in complex bond, or of a metal-containing formazane dyestuff.

In those compounds of Formula III in which D is the radical of an anthraquinone dyestuff, it is preferably a 1-amino-4-phenylamino- or 1-amino-4-diphenylamino-anthraquinone radical.

When D is the radical of a phthalocyanine dyestuff, it is preferably the radical of phthalocyanine sulfonic acid alkylamide or arylamide, which preferably contains sulfonic acid groups.

The organic dyestuffs of Formula I contain the



groups either in the internal, principal dyestuff structure or at an external substituent, such as at the benzene ring of benzoylamino or of phenylamino groups.

The dyestuffs mentioned can contain "shade- and fastness properties-influencing" substituents.

Such "shade- and fastness properties-influencing" types of substitution in the dyestuffs according to the invention are: fluorine, chlorine, bromine, lower alkyl groups having straight or branched chains such as the methyl, ethyl, propyl, isopropyl, n-butyl, tert. butyl and amyl group, cycloalkyl groups such as the cyclohexyl and the methyl cyclohexyl group, aralkyl groups such as the benzyl or phenethyl group, ether groups such as lower alkoxy, e.g. methoxy, ethoxy, or benzyloxy or phenoxy group, lower alkyl-sulfonyl, carboxylic acid and sulfonic acid groups, acylamino groups such as the acetylamino, chloroacetylamino, β-bromopropionylamino, phenylamino and benzoylamino group, carboxylic acid amide and sulfonic acid amide groups which may be N-substituted, also the nitro, amino, carbamido, amino-phenyl —SO_2—NH—SO_2 and hydroxyl groups.

R, when representing a lower alkyl group is, for example, the methyl or ethyl group; preferably, however, it represents hydrogen.

The reactivity of dyestuffs of Formula III according to the invention in which Hal is fluorine is superior to that of dyestuffs in which Hal is chlorine. They can thus be fixed onto the fiber at relatively low temperatures, whereas dyestuffs in which Hal is chlorine require higher fixing temperatures or stronger bases, e.g. sodium hydroxide, as acid-binding agents.

The lower alkyl substituent at the nitrogen atom in Formula III to which the triazinyl radical is attached is, for example, methyl, ethyl, isopropyl or butyl.

The monovalent electron-donating substituent X which is of a molecular weight not exceeding 200, and preferably below 150, represents, for example, ether groups such as an alkoxy group, e.g. the methoxy or the ethoxy group; an aryloxy group, in particular the unsubstituted phenoxy group, but also a phenoxy group substituted by halogen, e.g. chlorine, by lower alkyl or lower alkoxy; a thioether group, in particular a lower alkylthio group such as the methylthio group or ethylthio group as well as an arylthio group, in particular the unsubstituted phenylthio group or a phenylthio group substituted by halogen, e.g. chlorine, by lower alkyl or lower alkoxy. Especially, however, X represents an amino group derived from a primary or secondary organic, preferably aliphatic amine, in particular a monoalkylamino or dialkylamino group such as methylamino, ethylamino, propylamino, isopropylamino, butylamino, isobutylamino, tert. butylamino, dimethylamino, diethylamino, dipropylamino or dibutylamino.

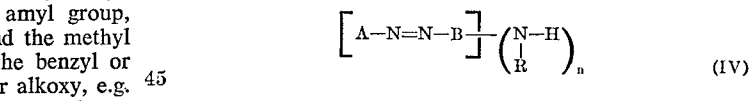
The lower mono- and di-alkylamino radicals are preferred on account of the higher solubility of the resulting reactive dyestuffs of Formula III.

In starting materials containing the grouping of Formula II, the lower di-alkylamino radicals are preferred because of the more uniform phosgenization in the synthesis of these starting materials. Furthermore, the radical X may be derived from saturated heterocyclic nitrogen bases such as piperidine or morpholine; or X may represent the radical of a phenylamino or N-lower-alkyl-N-phenylamino group the phenyl radical of which is unsubstituted or substituted by halogen, e.g. chlorine or bromine, or by lower alkyl or lower alkoxy.

Amino dyestuffs of Formula I, into the molecules of which the fiber-reactive grouping according to the invention can be introduced are, for example, amino-anthraquinones such as 1-amino-4-(m- or p-amino-phenylamino)- or 4-(o'-, m'- or p'-amino-diphenylamino)anthraquinones and their sulfonic acids; aminophthalocyanines such as condensation products of phthalocyanine sulfonic acid chloride with alkylene-diamines or with arylene-diamines which may be sulfonated; and also amino-azo dyestuffs as well as the sulfonic acids thereof. The latter contain acylatable amino groups

in the coupling component and/or in the diazo component.

For instance, aminoazo dyestuffs of the formula



(IV)

are particularly valuable starting materials. In this formula

A represents the radical of a diazo component, particularly a benzene diphenyl or naphthalene radical which is unsubstituted or bears a "shade- and fastness properties-influencing" substitution of the type further described hereinbefore,

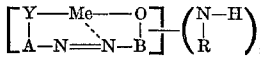
B represents the radical of a coupling component,

R and *n* have the same meanings as in Formula I.

Preferably A and B together contain at least two sulfonic acid groups.

The azo dyestuffs of Formula IV are obtained, for example, by coupling optionally sulfonated acylaminophenyl, acylaminodiphenyl or acylaminonaphthyl diazonium compounds or nitroaryldiazonium compounds, more particularly, for example, by coupling a diazotized acetylamino aniline, 4-acetylamino-4'-amino-1,1'-diphenyl or a nitroaniline which may contain sulfonic acid groups, with conventional coupling components, e.g. with those of the benzene, naphthalene, pyrazole or acyloacetylarylamide series, then saponifying the acylamino group or reducing the nitro group to the amino group. They are also obtained by coupling a diazonium compound with a coupling component containing acylatable amino groups, e.g. with an aminobenzene, aminonaphthalene or aminonaphthol, or also with an aminoaryl pyrazolone or aminoaryl pyrazole imine or with an acyloacetylarylamide or with their sulfonic acids.

Other valuable starting materials are metal-containing aminoazo dyestuffs of the formula



(V)

wherein

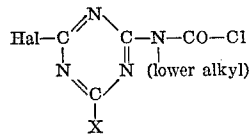
A represents a benzene or naphthalene radical which is unsubstituted or bears a "shade- and fastness properties-influencing" substitution, as described hereinbefore,
B represents the radical of a coupling component,
Me represents a heavy metal of the atomic numbers 2- to 29 which can also contain other co-ordinated complex formers,
Y represents oxygen or the —COO— group, and
R and *n* have the same meanings as in Formula I.

The bridge members Y and the oxygen atom in Formula V are linked to A and B, respectively, in ortho-position to the azo bridge, —N=N—.

Preferably, the aminoazo dyestuffs of Formula V contain at least two sulfonic acid groups.

Metallized aminoazo dyestuffs of this type are obtained, for example, by coupling optionally sulfonated acylaminophenyl or acylamino-naphthyl or nitrophenyl diazonium compounds which preferably contain a hydroxyl, alkoxy or carboxyl group in the o-position to the diazonium group, with conventional coupling components capable of coupling in a position adjacent to a hydroxyl group, e.g. phenols, naphthols, pyrazolones or acyloacetylarylamides, and also the sulfonic acids of these compounds. They are also obtained by coupling the usual aromatic diazonium compounds, particularly optionally sulfonated o-hydroxyaryl, o-alkoxyaryl or o-carboxyaryl diazonium compounds with coupling components capable of coupling in a position adjacent to a hydroxyl group, which coupling components may contain an acylated amino group, e.g. with an aminonaphthol or acylaminonaphthol, or with an aminonaphthol or acylaminonaphthol sulfonic acid. After the acylamino group has been hydrolyzed or the nitro group has been reduced to the amino group, the aminoazo compounds obtained are converted into heavy metal complexes with agents yielding chromium, cobalt, nickel or copper, if necessary in the presence of an oxidizing agent. To saturate any other co-ordination positions present, the dyestuffs according to the invention can also contain other complex-forming compounds which may have dyestuff character and are bound by way of the heavy metal, for example, water, certain tertiary amines such as pyridine or another o,o'-dihydroxy- or o-hydroxy-o'-carboxyazo dyestuff.

Compounds usable according to the invention which introduce the radical of Formula II, above, into the dyestuff starting materials of Formula I are mainly the carbamic acid chlorides of the formula

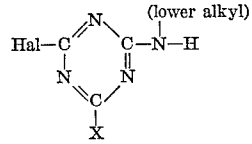


(VI)

wherein

Hal and X have the same meanings as in Formula II.

The carbamic acid chlorides of Formula VI are obtained by known processes, in particular by reacting halogen-amino-s-triazines compounds of the formula



(VII)

in which

X and Hal have the same meanings as in Formula II,

with phosgene in an inert organic solvent. Suitable solvents are, e.g. optionally halogenated or nitrated aromatic hydrocarbons such as toluene, chlorobenzene or nitrobenzene.

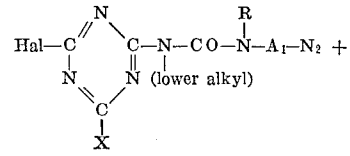
The reaction of an amino dyestuff of Formula I with the acylating agent introducing the radical of Formula II, preferably a compound of Formula VI, is advantageously performed in aqueous solution, optionally in the presence of inert organic solvents, e.g. lower alkanols, lower aliphatic ketones or lower fatty acid amides, if necessary in the presence of buffer salts or tertiary nitrogen bases such as dialkyl anilines as acid binding agents. To prevent a premature exchange of substituents which can be split off, the reaction is performed with care under mild conditions, preferably at a pH of 4 to 8 and at as low temperatures as possible. Mild conditions are also indicated for the isolation and drying of the reaction products.

Reactive dyestuffs of Formula III are also obtained by a modified process by forming them from dyestuff components which contain at least one radical of Formula II bound by way of an amino group



This method is particularly suitable for the production of azo dyestuffs and comprises coupling an aromatic diazonium compound with a coupling component, at least one of which contains the characteristic fiber-reactive acylamino group according to the invention.

For example, a diazonium compound of the formula

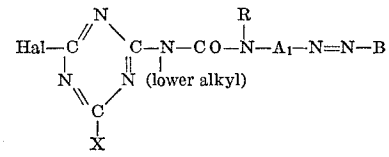


(VIII)

wherein

A_1 represents a benzene, diphenyl or naphthalene radical or an azo dyestuff radical, which may have further "shade- and fastness properties-influencing" substitution as described hereinbefore,
R has the same meaning as in Formula I, and
Hal and X have the same meanings as in Formula II,

is coupled with a coupling component B—H to form an azo dyestuff of the formula



(IX)

wherein

A_1 has the same meaning as in Formula VIII, and
B represents the radical of a coupling component;

if desired, metallizable dyestuffs thus obtained are then reacted with agents introducing a complex-forming heavy metal.

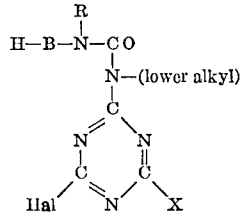
Diazonium compounds of Formula VIII used in this process are derived from optionally sulfonated arylenediamines, such as p- or m-phenylenediamine sulfonic acid or 2,6-naphthylene-diamine-4,8-disulfonic acid.

Components to be coupled therewith are those conventional in azo dyestuffs, for example, those of the benzene series such as phenols or anilines, of the naphthalene series such as optionally sulfonated naphthols, naphthylamines or phenyl- and acyl-aminonaphthols, furthermore, pyrazolones, pyrazole imines or acryloacetylarylamides.

A further method of performing the process for the production of reactive dyestuffs of Formula III comprises reacting an aryl diazonium compound

$$(A—N_2)^+(anion)^-$$

with a coupling component of the formula



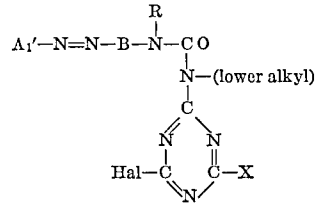
(X)

wherein

R has the same meaning as in Formula I, Hal and X have those given in Formula II and

B represents the radical of an azo dyestuff-forming coupling component,

to produce a dyestuff of the formula wherein



(XI)

B, Hal, R and X have the same meanings as in Formula X and

—A_1' in the diazo component A_1'—N=N— represents, a radical of the benzene, diphenyl, naphthalene

or azo dyestuff series which may be further substituted, and, if desired, converting a dyestuff thus obtained which possesses metallizable substituents in A_1' and B, to a heavy metal complex thereof, with agents giving off heavy metal.

Diazotized aromatic amines usual in azo dyestuffs are used in this process as diazonium compounds, for example, optionally sulfonated phenyl, diphenyl, naphthyl or azo dyestuff diazonium compounds. The latter are especially benzene-azo-benzene-diazonium, benzene-azo-naphthalene - diazonium, or naphthalene - azo - benzene-diazonium compounds.

In Formula X, B, the radical of the coupling component of the dyestuff of Formula XI, represents, for example, the radical of an aminonaphthol sulfonic acid such as the radical of a 1-amino-6- or -7-hydroxynaphthalene sulfonic acid, of 1-amino-8-hydroxynaphthalene-3,6- or 4,6-disulfonic acid, of 2-amino-8-hydroxynaphthalene-6-sulfonic acid, or the radical of an optionally sulfonated aminoaryl pyrazolone or pyrazole imine or of an acylacetylarylamide.

Azo dyestuffs containing two radicals of Formula II are obtained, for example, by coupling a diazonium compound of Formula VIII with a coupling component of Formula X.

The coupling is performed in every case in a weakly acid to weakly alkaline medium by the usual methods.

Both the coupling and the metallization must be performed under mild conditions, i.e. high pH values and temperatures should be avoided.

The dyestuffs obtained can be stabilized with buffer substances, for example with mixtures of primary and secondary alkali phosphates or with alkali metal salts of sulfonated tertiary aromatic amines, that is, for example, with the sodium salt of N,N-dimethylaniline-3-sulfonic acid.

The preferred dyestuffs of Formula III contain water solubilizing, salt-forming groups and are suitable for the dyeing of natural and synthetic polyamide fibers containing amino groups. An after-treatment of the dyeing with acid-binding agents such as ammonia or hexamethylenetetramine improves the wet fastness properties, especially of dyeings on wool.

Water soluble reactive dyestuffs according to the invention which correspond to Formula II and contain

advantageously two to five sulfonic acid groups are mainly used, however, for the dyeing and printing of textile fibers containing hydroxyl groups, particularly for natural or regenerated cellulose fibers. Dyeings and prints are obtained which are distinguished by excellent wet fastness properties and good fastness to light by impregnating the textiles with aqueous dyestuff solutions or printing them with thickened dyestuff solutions, drying the impregnated material and treating with acid binding agents, optionally with heating or steaming, and then thoroughly rinsing and soaping.

The dyestuffs according to the invention are also suitable for the dyeing of fibers containing hydroxyl groups by the exhaustion process. During or after the dyeing process which, advantageously, is promoted by the addition of neutral salts such as sodium sulfate or sodium chloride, the dyestuff is fixed by treatment with acid binding agents. A particularly simple dyeing process consists in adding the total amount of the neutral salts which promote exhaustion and adding the acid binding agent to the dyebath from the very beginning, introducing the goods to be dyed at low temperatures (25–40° C.) into the bath, heating the bath gradually to a temperature, depending on the aforementioned starting temperature, in the range of from 40 to 100° C., and continuing treatment at the latter temperature until the fixation of the dyestuff is completed. In this way, dyeings having excellent wet fastness properties and good fastness to light are obtained.

Reactive dyestuffs of Formula III wherein Hal is chlorine are fixed at room temperature (about 20° C.) when the bath is strongly alkaline (pH above 11) or, preferably, at elevated temperatures (60 to 160° C.) at lower pH (about 9 to 11) and those in which Hal represents fluorine are fixed under milder conditions, e.g. at lower temperatures (20 to 30° C.) and/or lower pH (8–11), or correspondingly shorter time.

"Wet fastness" properties shown by the dyestuffs according to the first and also by those of the second aspect of this invention, described in detail hereinafter, are, in particular, wash fastness, fastness to water, to sea water, to perspiration, and, in the case of wool dyeings, also fastness to milling and potting. These wet fastness properties are also found in wool dyeings of stronger shades (e.g. standard depths 2 to 5).

Moreover, the yield rate of fixed dyestuff to unfixed dyestuff portion on wool is very favorable in the case of dyestuffs of the first as well as of the second aspect of the invention.

In the dyeing of cotton and the like cellulose fibers, the unfixed portion of these dyestuffs remaining on the fibers after fixation, can be very readily removed by washing with hot water or by soaping. Wool dyeings are distinguished by level strike of these dyestuffs irrespective of differences in the type of wool, which levels strike is assured especially by the use of anionic or non-ionogenic dyestuff carriers or mixtures of such carriers.

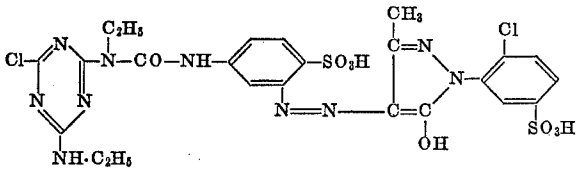
Preferably sodium or potassium bicarbonate, sodium or potassium carbonates, sodium metasilicate, trisodium phosphate or sodium hydroxide solution, or the sodium or potassium salt of trichloroacetic acid are used as acid binding agents. In addition the dye liquor or printing paste can contain further additives, for example salts such as sodium sulfate or chloride already mentioned, or auxiliaries such as acid amides, e.g. urea or additives which prevent reduction such as nitrobenzene sulfonic acid, and also additives which accelerate the reaction, such as tertiary amines, e.g. trimethylamine or 1,4-diaza-bicyclo-(2,2,2)-octane.

Reactive dyestuffs according to the invention which correspond to Formula III and which contain no sulfonic acid group are preferably used in fine aqueous dispersion for the dyeing of hydrophobic fibers, in particular for the dyeing of synthetic polyamide fibers such as nylon.

Further details can be seen from the following non-

limitative examples of this aspect of the invention. Where otherwise expressly stated, parts and percentages are given by weight. The temperatures are in degrees centigrade. The relationship of parts by weight to parts by volume is as that of grams (g) to milliliters (ml.).

EXAMPLE 1



18.8 parts of 1,3-diaminobenzene-4-sulphonic acid are dissolved in 400 parts of water with the addition of sodium carbonate to give a pH of 4.0–4.5, and the solution is cooled to 0–5°. 27.7 parts of 2-ethylamino-4-N-chloroformyl-ethylamino-6-chloro-s-triazine dissolved in 100 parts of acetone are added dropwise at this temperature within 15 minutes, the pH of the reaction mixture being maintained at 4.0–4.5 by the simultaneous addition of sodium carbonate solution. As soon as the reaction is completed, 25 parts of aqueous 30% hydrochloric acid are added and diazotisation is performed with 6.9 parts of sodium nitrite at 0–5°. The suspension of the diazonium compound is poured into a solution of the sodium salt of 28.9 parts of 1-(2'-chloro-5'-sulphophenyl)-3-methyl-5-pyrazolone in 200 parts of water and 40 parts of sodium acetate. On completion of the couplings, the new dyestuff is precipitated with sodium chloride, filtered off, washed with dilute sodium chloride solution and dried in vacuo at 40–50°. It is a yellow powder which dissolves in water with a greenish yellow colour.

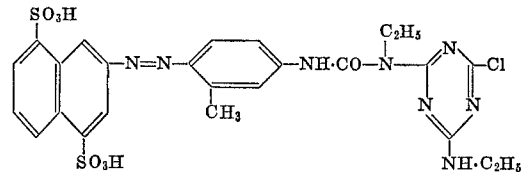
The new dyestuff dyes cotton, staple fibre, jute, ramie, hemp, wool, silk and nylon by the processes usual for reactive dyestuffs in pure yellow shades which are fast to wet and light.

Dyestuffs having similar properties are obtained when, instead of the 1-(2'-chloro-5'-sulfophenyl)-3-methyl-5-pyrazolone, an equivalent amount of the coupling components given in the following Table 1 are used.

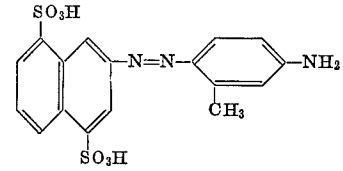
TABLE 1

Example No.	Coupling component	Shades
2	1-(2',5'-disulfophenyl)-3-methyl-5-pyrazolone.	Yellow.
3	1-[5',7'-disulfonaphthyl-(2')]-3-methyl-5-pyrazolone.	Do.
4	1-(4'-sulfophenyl)-5-pyrazolone-3-carboxylic acid.	Do.
5	1-(3'-sulfophenyl-3-methyl-5-pyrazolone	Do.
6	1-(2'-fluoro-5'sulfophenyl)-3-methyl-5-pyrazolone.	Do.
7	1-chloroacetylamino-8-hydroxynaphthalene-4,6-disulfonic acid.	Red.
8	1-(β-bromopropionylamino)-8-hydroxy-naphthalene-3,6-disulfonic acid.	Red.

EXAMPLE 9



42.1 parts of the aminomonoaza dyestuff of the formula



(produced by diazotizing 2-aminonaphthalene-4,8-disulfonic acid and coupling the diazonium compound with 1-amino-3-methylbenzene in the presence of alkali metal salts of fatty acids) are dissolved in the form of the sodium salt in 400 parts of water. 29.1 parts of 2-ethylamino-4-N-chloroformyl-ethylamino - 6 - chloro-s-triazine dissolved in 100 parts of acetone are added dropwise at 20–25° within 1 hour, the pH of the reaction mixture being kept at 6.5–7.0 by the simultaneous addition of sodium carbonate solution. As soon as no more free amino groups can be traced, the reaction product is precipitated by the addition of sodium chloride, filtered off and washed with dilute sodium chloride solution. The new dyestuff is dried in vacuo at 40–50°. It is a yellow powder which dissolves in water with a yellow color. It dyes cellulose and polyamide fibers by the processes usual for reactive dyestuffs in pure yellow shades which have good fastness to wet and light.

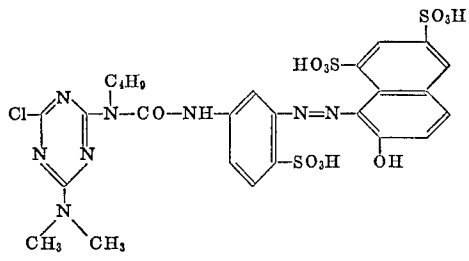
Other azo dyestuffs having similar properties are obtained by reacting equivalent amounts of the aminoazo dyestuffs given in the following Table 2, in accordance with Example 9 with

(a) 29.1 parts of 2-ethylamino-4-N-chlorofromyl ethylamino-6-chloro-s-triazine or with equivalent parts of the reactants indicated in column 3 of the table, namely
(b) 2 - dimethylamino-4-N-chloroformyl - ethylamino-6-chloro-s-triazine,
(c) 2 - N-methyl-N-phenylamino-4-N-chloroformylmethylamino-6-chloro-s-triazine,
(d) 2 - ethylamino-4-N-chloroformyl - ethylamino-6-fluoro-s-triazine,
(e) 2-(4'-chlorophenoxy) - 4 - N - chloroformyl-methylamino-6-bromo-s-triazine, or
(f) 2-propylamino-4-N-chloroformyl - methylamino-6-chloro-s-triazine.

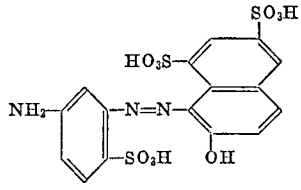
TABLE 2

Example No.	Aminoazo dyestuff	Reactant	Shade on cellulose fibers
10	2-aminonaphthalene-5,7-disulfonic acid → aniline.	a, b, c, d, e, f	Yellow.
11	2-aminonaphthalene-4,8-disulfonic acid → 2-methoxy-5-methylaniline.	a, b, c, d, e, f	Do.
12	2-aminonaphthalene-4,6,8-trisulfonic acid → aniline.	a, b, c, d, e, f	Do.
13	2-aminonaphthalene-4,6,8-trisulfonic acid → 3-methyl-1-aminobenzene → aniline.	a, b, c, d, e, f	Orange.
14	4-aminoazobenzene-3,4'-disulfonic acid → 3-methyl-1-aminobenzene.	a, b, c, d, e, f	Do.
15	2-aminonaphthalene-4,8-disulfonic acid → N-methylaniline.	a, b, c, d, e, f	Yellow.
16	1-aminobenzene-2,4-disulfonic acid → 1-aminonaphthalene-6-sulfonic acid → 1-methyl-3-aminobenzene.	a, b, c, d, e, f	Orange.
17	1-aminobenzene-2,5-disulfonic acid → m-aminophenyl urea.	a, b, c ,d, e, f	Yellow.

EXAMPLE 18



50.3 parts of the amino azo dyestuff of the formula



(produced by coupling diazotized 2 - amino-4-acetylaminobenzene-1-sulfonic acid with 2 - hydroxynaphthalene-6,8 - disulfonic acid in an alkaline medium and saponifying the acetylamino group with sodium hydroxide solution, in accordance with the procedure described by Fierz-David and Blangey in "Farbenchemie," 8th edition, page 283 et seq.) are dissolved, in the form of the sodium salt, in 800 parts of water with a neutral reaction. 30.6 parts of 2-dimethylamino-4-N-chloroformyl-n-butylamino-6-chloro-s-triazine dissolved in 100 parts of acetone are added at 15–20° the pH of the reaction mixture being kept at 5–5.5 by the addition dropwise of sodium carbonate solution. As soon as no more diazotizable amino groups can be traced, the dyestuff is completely precipitated by the addition of sodium chloride, filtered off and dried in vacuo at 60–70°. It dissolves easily in water with an orange color and dyes polyamide and cellulose fibers by the processes usual for reactive dyestuffs in yellowish orange shades.

By reacting the aminoazo dyestuffs listed in the following Table 3 according to the procedure described in Example 18 with, in each case,

(a) 2-dimethylamino-4-N-chloroformyl-n-butylamino-6-chloro-s-triazine or with equivalent parts of
(b) 2-methoxy-4-N-chloroformyl-ethylamino-6-chloro-s-triazine,
(c) 2-phenoxy-4-N-chloroformyl-methylamino-6-chloro-s-triazine,
(d) 2-morpholino-4-N-chloroformyl-methylamino-6-bromo-s-triazine,
(e) 2-(4'-methoxy-phenoxy)-4-N-chloroformyl-ethylamino-6-chloro-s-triazine,
(f) 2-(4'-chlorophenylamino)-4-N-chloroformyl-methylamino-6-chloro-s-triazine and
(g) 2-dimethylamino-4-N-chloroformyl-methylamino-6-chloro-s-triazine,

respectively valuable dyestuffs are obtained, dyeings of which on cellulose fibers yield the shades given in the last column of Table 3 below.

TABLE 3

Example No. (a-g)	Aminoazo dyestuffs	Shade on cellulose fibers
19	2-amino-4-nitrobenzene sulphonic acid → 1-acetylamino-8-hydroxynaphthalene-3,6-disulphonic acid, reduced.	Red.
20	2-amino-4-nitrobenzene sulphonic acid → 1-benzoylamino-8-hydroxynaphthalene-3,6-disulphonic acid, reduced.	Red.
21	2-amino-4-acetylaminobenzene sulphonic acid → 1-hydroxynaphthalene-3,6-disulphonic acid, saponified.	Orange.
22	2-amino-4-acetylaminobenzene sulphonic acid → 1-hydroxynaphthalene-4,6-disulphonic acid, saponified.	Red-orange.
23	1-aminobenzene-2,5-disulphonic acid alkaline ⟶ 2-amino-5-hydroxynaphthalene-7-sulphonic acid.	Orange.
24	2-aminonaphthalene-1,5-disulphonic acid alkaline ⟶ 2-methylamino-5-hydroxy-naphthalene-7-sulphonic acid.	Reddish orange.
25	1-aminobenzene-2,4-disulphonic acid → 1-(3'-aminobenzoylamino)-8-hydroxy-naphthalene-3,6-disulphonic acid.	Red.
26	2-amino-4-acetylaminobenzene sulphonic acid → 2-aminonaphthalene-5,7-disulphonic acid, saponified.	Orange.
27	2-amino-4-acetylaminobenzene sulphonic acid → 1-(3'-sulphophenyl)-3-methyl-5-pyrazolone, saponified.	Yellow.
28	2-amino-5-nitrobenzene sulphonic acid → 1-(3'-sulphophenyl)-3-methyl-5-pyrazole imine, reduced.	Do.
29	1-amino-3-nitro-6-ethylbenzene → 1-hydroxy naphthalene-3,6-disulfonic acid, reduced.	Reddish orange.
30	1-amino-3-N-methylsulfamylbenzene → 1-amino-8-hydroxynaphthalene-3,6-disulfonic acid.	Red.
31	1-aminobenzene-3-N-(γ-hydroxypropyl)-N-methylsulfonamide → 1-amino-8-hydroxynaphthalene-3,6-disulfonic acid.	Red.
32	4-amino-3-carboxy-benzene-sulfonic acid → 2-amino-5-hydroxynaphthalene-7-sulfonic acid.	Orange.
33	1-aminobenzene-3-N-(β-hydroxyethyl)-N-methylsulfonamide → 1-amino-8-hydroxynaphthalene-4,6-disulfonic acid.	Red.
34	3-amino-4-ethoxybenzene-sulfonic acid → 2-amino-5-hydroxynaphthalene-7-sulfonic acid.	Orange.
35	1-aminobenzene-3-N-(β-sulfoethyl)-N-methylsulfonamide → 1-amino-8-hydroxy-naphthalene-3,6-disulfonic acid.	Red.
36	2-aminonaphthalene-4,6,8-trisulfonic acid → 1-(4'-aminophenyl)-3-methyl-5-pyrazolone.	Yellow.
37	1-amino-3-N,N-bis-(γ-hydroxypropyl)-sulfamyl-benzene → 1-amino-8-hydroxy-naphthalene-3,6-disulfonic acid.	Red.
38	2,3'-diamino-diphenyl-1,1'-disulfimide → 1-amino-8-hydroxynaphthalene-3,6-disulfonic acid.	Red.
39	2-aminonaphthalene-1,5,7-trisulfonic acid → 2-amino-5-hydroxynaphthalene-7-sulfonic acid → 1-amino-3-methylbenzene.	Red.
40	2-amino-4-nitrobenzene sulfonic acid → 1-benzoylamino-8-hydroxynaphthalene-4,6-disulfonic acid, reduced.	Red.

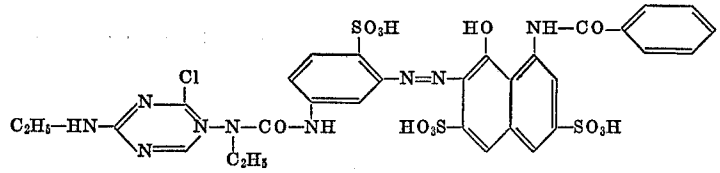
As used in the above Table 3 and subsequent tables

"alkaline" ⟶

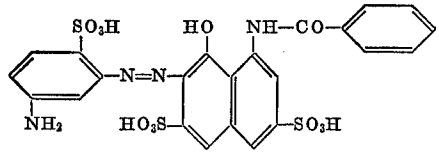
means that the coupling was carried out in a conventional manner at a pH above 7, "saponified" means that the coupled product was treated as described in Exam-

ple 18, supra, and "reduced" means that the coupling product was treated as described in Example 40h, infra.

EXAMPLE 40h

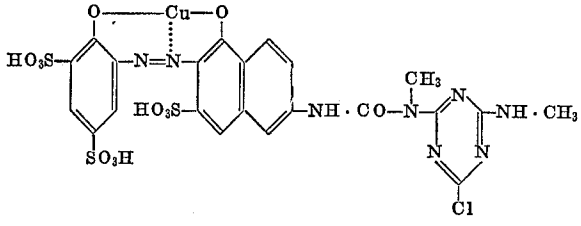


62.2 parts of the sodium salt of the aminoazo dyestuff of the formula

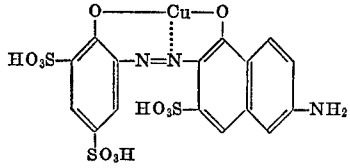


(obtained by coupling diazotized 2-amino-4-nitrobenzene sulfonic acid with 1-benzoylamino-8-hydroxynapthalene-3,6-disulfonic acid in a neutral medium and reducing the nitroazo dyestuff with sodium sulfide in alkaline medium of pH about 10–12) are dissolved in 500 parts of water. At 15–20°, 29.0 parts of 2-ethylamino-4-N-chloroformyl-ethylamino-6-chloro-s-triazine dissolved in 100 parts of acetone are added dropwise, the pH of the reaction solution being kept at 5.0–5.5 by the addition of sodium carbonate solution. As soon as no more free amino groups can be detected, the dyestuff is completely precipitated by the addition of sodium chloride, filtered off and dried in vacuo at 60–70°. It dissolves easily in water with a red color and dyes cellulose and polyamide fibers by processes usual for reactive dyestuffs in pure red shades.

EXAMPLE 41



51.7 parts of the copper containing aminomonazo dyestuff of the formula



(obtained by coupling diazotised 2-amino-1-hydroxy-benzene-4,6-disulphonic acid with 2-amino-5-hydroxy-naphthalene-7-sulphonic acid in an alkaline medium and treating the aminomonoazo dyestuff obtained with an agent giving off copper) are dissolved, in the form of the sodium salt, in 1000 parts of water. At 0–10°, a solution of 27.6 parts of 2-methylamino-4-N-chloroformyl-methyl-amino-6-chloro-s-triazine in 150 parts of actone is added and the pH of the reaction solution is maintained at 5.5–6.0 by the addition of sodium carbonate solution. As soon as no more free amino groups can be traced, the new dyestuff is completely precipitated by the addition of sodium chloride, filtered off and dried in vacuo at 40–50°. It is a dark powder which dissolves in water with a ruby red color.

It dyes cotton, staple fiber, jute, ramie, hemp, wool, silk and nylon by the processes usual for reactive dyestuffs in pure ruby red shades which are wet fast.

Further metal-containing aminoazo dyestuffs are given in the following Table 4 which are reacted as described in this example with

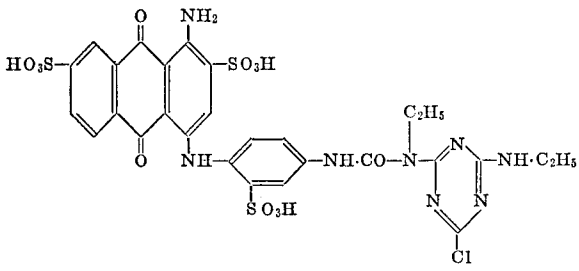
(a) 2-methylamino-4-N-chloroformyl-methylamino-6-chloro-s-triazine or with equivalent parts of
(b) 2-ethylamino-4-N-chloroformyl-ethylamino-6-chloro-s-triazine,
(c) 2-ethoxy-4-N-chloroformyl-methylamino-6-chloro-s-triazine,
(d) 2-phenylthio-4-N-chloroformyl-methylamino-6-chloro-s-triazine,
(e) 2-amylamino-4-N-chloroformyl-butylamino-6-chloro-s-triazine and
(f) 2-(4'-methylphenylthio)-4-N-chloroformyl-methylamino-6-chloro-s-triazine,

respectively. The shades of dyeings with the end products on cellulose fibers are given in the last column of Table 4.

TABLE 4

Example No. (a–f)	Metal-containing aminoazo dyestuffs	Shade on cellulose fibres
42	2-amino-1-hydroxybenzene-4,6-disulphonic acid —alkaline→ 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid, copper complex.	Violet.
43	2-amino-1-hydroxybenzene-4-sulphonic acid —alkaline→ 2-amino-8-hydroxynaphthalene-6-sulphonic acid, copper complex.	Bordeaux.
44	6-nitro-1-amino-2-hydroxynaphthalene-4-sulphonic acid —alkaline→ 2-amino-5-hydroxynaphthalene-7-sulphonic acid, chromium complex 1:2.	Black.
45	4-nitro-2-amino-1-hydroxybenzene —alkaline→ 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid, chromium complex 1:2.	Do.
46	4-nitro-2-amino-1-hydroxybenzene —alkaline→ 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid, cobalt complex 1:2.	Black-brown.
47	2-amino-4-acetylamino-1-hydroxybenzene-6-sulphonic acid —alkaline→ 1-amino-8-hydroxynaphalene-2,4-disulphonic acid, copper complex, saponified.	Reddish navy blue.
48	2-amino-4-acetylamino-1-hydroxybenzene-6-sulphonic acid —alkaline→ 1-phenylamino-8-hydroxynaphthalene-4,6-disulphonic acid, copper complex, saponified.	Navy blue.
49	6-nitro-1-amino-2-hydroxynaphthalene-4-sulphonic acid —alkaline→ 1-amino-8-hydroxynaphthalene-2,4-disulphonic acid, reduced, copper complex.	Blue.
50	2-amino-6-acetylamino-1-hydroxybenzene-4-sulphonic acid → 1-hydroxynaphthalene-4,6-disulphonic acid, copper complex, saponified.	Ruby red.
51	2-amino-6-acetylamino-1-hydroxybenzene-4-sulphonic acid → 1-(2',5'-disulphophenyl)-3-methyl-5-pyrazolone, copper complex, saponified.	Yellow brown.
52	1-hydroxy-2-amino-5-methylsulfonylbenzene → 2-amino-8-hydroxynaphthalene-3,6-disulphonic acid, copper complex.	Ruby.
53	3-amino-4-hydroxy-benzolsulfonic acid → N-(3'-aminophenyl)-acetoacetic acid amide 1:2-cobalt complex.	Yellow.
54	3-hydroxy-4-amino-bromobenzol → 1-amino-8-hydroxynaphthalene-3,6-disulfonic acid, copper complex.	Violet.
55	1-hydroxy-2-amino-benzene-5-N-(β-methoxyethyl)-N-amylsulfonamide → 2-amino-8-hydroxynaphthalene-3,6-disulfonic acid, copper complex.	Ruby.

EXAMPLE 56



56.9 parts of 1-amino-4-(4'-aminophenylamino)-anthraquinone-2,2',7'-trisulphonic acid (obtained by sulphonation of 1-amino-4-(4'-aminophenylamino)-anthraquinone-2,7-disulphonic acid in 30% oleum) are dissolved, in the form of the sodium salt, in 1000 parts of water. A solution of 27.7 parts of 2-ethylamino-4-N-chloroformyl-ethylamino-6-chloro-s-triazine in 100 parts of acetone is added to this solution dropwise at 20–25° and the pH is maintained at 5.0–5.5 by the simultaneous addition of aqueous sodium carbonate solution. On completion of the reaction, the new dyestuff of the above formula is precipitated by the addition of sodium chloride, filtered off, washed with

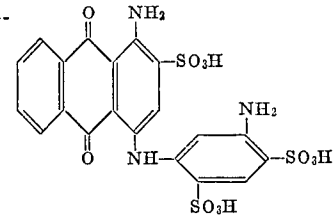
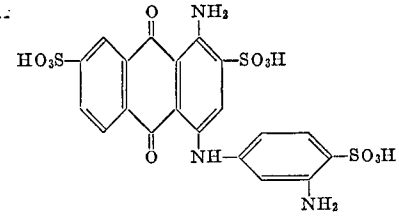
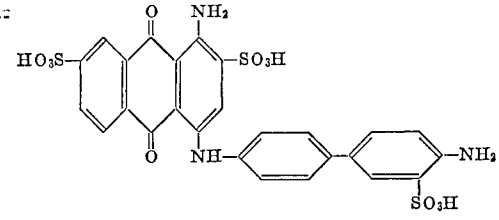
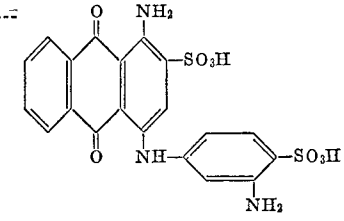
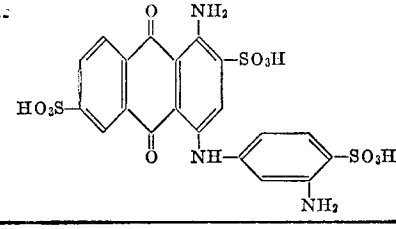
aqueous sodium chloride solution and dried in vacuo at 40–50°. It dissolves in water with a blue color and dyes cotton, staple fiber, jute, ramie, hemp, wool, silk and nylon by the processes usual for reactive dyestuffs in wet fast blue shades.

Other aminoanthraquinone dyestuffs listed in the following Table 5 are condensed as described in Example 56 with

(a) 2-ethylamino-4-N-chloroformyl-ethylamino-6-chloro-s-triazine or with equivalent parts of
(b) 2-methylthio-4-N-chloroformyl-methylamino-6-chloro-s-triazine,
(c) 2-diethylamino-4-N-chloroformyl-methylamino-6-chloro-s-triazine,
(d) 2-N-methyl-N-(4'-chlorophenylamino)-4-N-chloroformyl-butylamino-6-chloro-s-triazine,
(e) 2-N-methyl-N-(4'-ethoxyphenylamino)-4-N-chloroformyl-methylamino-6-chloro-s-triazine, and
(f) 2-phenylamino-4-N-chloroformyl-ethylamino-6-chloro-s-triazine,

respectively. The shade of the cellulose dyeings obtained with the resulting reactive dyestuffs is given in the last column of Table 5.

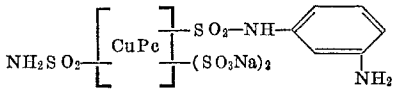
TABLE 5

Example No.	Aminoanthraquinone dyestuff	Shade on cellulose fibres
57		Blue.
58		Do.
59		Do.
60		Do.
61		Do.

EXAMPLE 62

57.6 parts of copper phthalocyanine tetrasulphonic acid chloride are slurried in 500 parts of water and 300 parts of ice. 15 parts of m-aminoacetanilide are stirred in and the pH is adjusted to 7 by the addition of aqueous ammonia solution. The temperature is allowed to rise slowly to 40–50°, the pH of the suspension being maintained at 7.0–7.5 by the dropwise addition of ammonia solution. As soon as no more primary amine can be traced, 270 parts of 30% hydrochloric acid are added and the mixture is heated for 3 hours at 85–90°. In this way the acetyl amino group is saponified.

The amino-phthalocyanine dyestuff of the formula

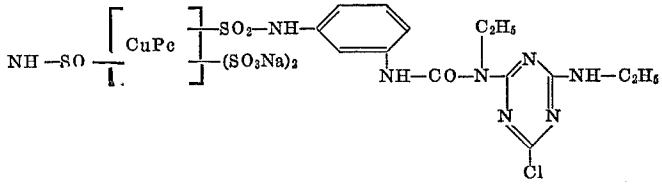


wherein

Pc represents the phthalocyanine structure

is so obtained.

This dyestuff is then isolated by filtration, again slurried in 1000 parts of 0–5° cold water and the pH of the suspension is adjusted to 8.0 with dilute sodium hydroxide solution. A solution of 27.7 parts of 2-ethylamino-4-N-chloroformyl-ethylamino-6-chloro-s-triazine in 100 parts of acetone is poured into this suspension. Condensation is performed at 15–20° while stirring well and the hydrochloric acid liberated is neutralised by the dropwise addition of dilute sodium carbonate solution. On completion of the reaction, the new dyestuff is completely salted out, filtered off and dried in vacuo at 50–60°. It corresponds to the formula



wherein

Pc represents the phthalocyanine structure.

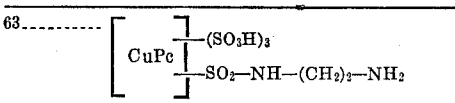
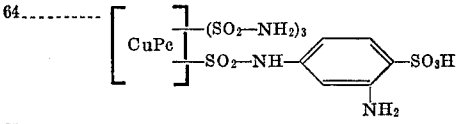
It dyes cellulose or polyamide fibres in wet fast, pure turquoise blue shades.

Other amino-phthalocyanine dyestuffs which are given in the following Table 6, are condensed as described in Example 62 with

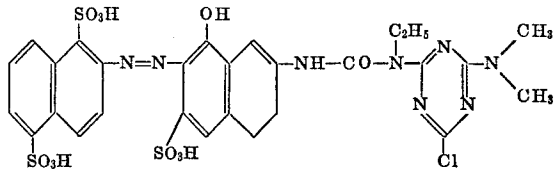
(a) 2-ethylamino-4-N-chloroformyl-ethylamino-6-chloro-s-triazine, or with equivalent parts of
(b) 2-piperidino-4-N-chloroformyl-methylamino-6-chloro-s-triazine,
(c) 2-dimethylamino-4-N-chloroformyl-ethylamino-6-chloro-s-triazine,
(d) 2-dibutylamino-4-N-chloroformyl-methylamino-6-chloro-s-triazine,
(e) 2-(4'-methylphenylamino)-4-N-chloroformyl-methylamino-6-chloro-s-triazine, and
(f) 2-N-methyl-N-(4'-methylphenylamino)-4-N-chloroformyl-methylamino-6-bromo-s-triazine,

respectively.

TABLE 6

Example No. (a-f)	Amino-phthalocyanine dyestuff	Shade on cellulose fiber
63		Turquoise blue.
64		Do.

EXAMPLE 65



23.9 parts of 2 - amino - 8 - hydroxynaphthalene-6-sulphonic acid are dissolved in 400 parts of 15–20° warm water and the pH is adjusted to 6.5 with sodium hydroxide solution. A solution of 30.6 parts of 2-N-methyl-N-ethyl-amino - 4-N-chloroformyl-ethylamino-6-chloro-s-triazine in 100 parts of acetone is added dropwise to this solution within 15 minutes and the pH of the reacting mixture is kept at 4.5–5.5 by the addition of sodium carbonate solution. When no more diazotisable amino groups can be traced, 30 parts of sodium bicarbonate are added to the solution and then a solution of 30.3 parts of diazotised 2 - aminonaphthalene - 1,5 - disulphonic acid is poured in. As soon as the coupling is completed sodium chloride is added to the reaction mixture, the precipitated dyestuff is filtered off and washed with sodium chloride solution. After drying at 60–70°, a red powder is obtained which dissolves easily in water with a red colour.

If cotton or staple fibre is dyed or printed by the processes usual for reactive dyestuffs, with this dyestuff then red dyeings or prints are obtained which have very good properties.

Other dyestuffs having similar properties are obtained if the coupling components containing acylatable amino groups given in the following table are condensed as described in Example 65 with

(a) 2 - N - methyl - N - ethylamino - 4 - N - chloroformylethylamino-6-chloro-s-triazine,

or with equivalent parts of

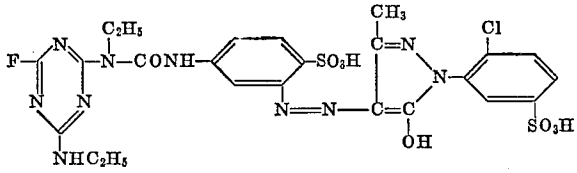
(b) 2-ethylamino-4-N-chloroformyl-ethylamino-6-fluoro-s-triazine,

and coupled with the diazo components also given in the Table 7.

TABLE 7

Example No. (a-b)	Diazo component	Coupling components containing acylatable amino groups	Shade of cotton
66	1-aminobenzene-2,5-disulphonic acid	1-amino-8-hydroxynaphthalene-3,6-disulphonic acid	Red.
67	2-aminonaphthalene-1,5-disulphonic acid	do	Blue is red.
68	1-aminobenzene-2-sulphonic acid	1-amino-8-hydroxynaphthalene-4,6-disulphonic acid	Red.
69	1-aminobenzene-2,4-disulphonic acid	1-(4'-aminophenyl)-3-methyl-5-pyrazolone	Yellow.
70	1-aminobenzene-2,5-disulphonic acid	2-amino-5-hydroxynaphthalene-7-sulphonic acid	Orange.
71	4-aminoazobenzene-3,4'-disulphonic acid	2-methylamino-4-hydroxynaphthalene-7-sulphonic acid	Scarlet.
72	2-aminonaphthalene-1,5-disulphonic acid	1-amino-8-hydroxynaphthalene-4,6-disulphonic acid	Blue is red.

EXAMPLE 73



18.8 parts of 1,3-diaminobenzene-4-sulphonic acid are dissolved in 400 parts of water and the pH is adjusted to 4.0–4.5 with sodium carbonate. 26 parts of 2-ethylamino-4-N-chloroformyl-ethylamino - 6 - fluoro-s-triazine dissolved in 100 parts of acetone and an aqueous sodium carbonate solution are added simultaneously to this solution within 15 minutes at 0–5° in such a way that the pH of the reaction mixture remains between 4.0 and 4.5. On completion of the reaction, 25 parts of 30% hydrochloric acid are added to the condensation product which is then diazotised at 0–5° with 6.9 parts of sodium nitrite. The suspension of the diazonium compound is poured into a solution of the sodium salt of 28.9 parts of 1-(2'-chloro-5'-sulphophenyl)-3-methyl-5 - pyrazolone in 200 parts of water and 4 parts of sodium acetate. As soon as the coupling is complete the pH of the dyestuff solution is raised to 7.0 and the new dyestuff is precipitated by the addition of sodium chloride. Also 19.5 parts of a mixture of anhydrous primary potassium phosphate and anhydrous secondary sodium phosphate in a weight ratio of 1.8:1.0 are added.

The mixture is stirred for 1 hour and the precipitate is filtered off, washed, and mixed with 11.7 parts of the mixture of anhydrous primary potassium phosphate and anhydrous secondary sodium phosphate mentioned above and dried in vacuo at a temperature under 45°.

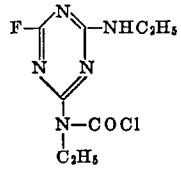
The monoazo dyestuff so obtained is a yellow powder which dissolves in water with a greenish yellow colour.

The 2 - ethylamino - 4 - N - chloroformyl-ethylamino-6 - fluoro-s-triazine used as starting material is obtained by reacting 2,4 - bis-ethylamino-6-chloro-s-triazine with potassium fluoride in dimethyl formamide to form 2,4-bis-ethylamino-6-fluoro-s-triazine and treating the latter according to known methods with phosgene in toluene.

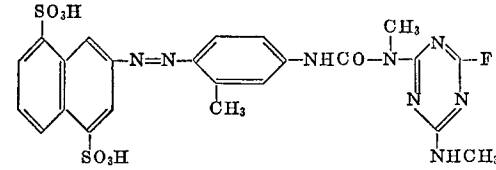
By padding cotton at room temperature with a 2% aqueous solution of this dyestuff which also contains 20 parts of sodium carbonate and 50 parts of sodium sulphate per litre, rolling up the impregnated goods, wrapping in a plastic cover and keeping for 4 hours at 25–30° and finally soaping at the boil for 30 minutes, then a yellow dyeing is obtained which has very good fastness to washing and light.

Dyestuffs having similar properties are obtained, in accordance with the preceding example, by condensing the diaminobenzene sulfonic acid compounds given in column II of the following Table 8 with equivalent parts of the acylating agents given in column II of said table; the condensation products are then diazotized and the resulting diazonium compounds are finally coupled with the coupling components listed in column IV. The shade on cellulose fibers obtained with thefinal products is given in the last column of Table 8.

TABLE 8

Example No.	II Diaminobenzene sulphonic acid compound	III Acylating agent	IV Coupling component	V Shade on cellulose fibres
74	1,3-diaminobenzene-4-sulphonic acid		1-(2',5'-disulphophenyl)-3-methyl-5-pyrazolone.	Yellow.
75	do	Same as above	1-(2',5'-dichloro-4'-sulphophenyl)-3-methyl-5-pyrazolone.	Do.
76	do	do	1-(3'-sulphophenyl)-3-methyl-5-pyrazolone.	Do.
77	do	do	1-[5',7'-disulphonaphthyl-(2')]-3-methyl-5-pyrazolone.	Do.
78	do	do	1-[4',8'-disulphonaphthyl-(2')]-3-methyl-5-pyrazolone.	Do.
79	do	do	1-(4'-sulphophenyl)-5-pyrazolone-3-carboxylic acid.	Do.
80	1,4-diaminobenzene-3-sulphonic acid	do	do	Do.
81	1,4-diaminobenzene-3-sulfonic acid	2-dimethylamino-4-N-chloroformyl-methylamino-6-fluoro-s-triazine.	1-(4'-sulfophenyl)-5-pyrazolone-3-carboxylic acid.	Do.
82	1,3-diaminobenzene-4-sulfonic acid	do	do	Do.
83	do	2-propylamino-4-N-chloroformylmethyl-amino-6-fluoro-s-triazine.	1-(2',5'-disulfophenyl)-3-methyl-5-pyrazolone.	Do.
84	do	2-ethylthio-4-N-chloroformylbutylamino-6-fluoro-s-triazine.	1-(2',5'-dichloro-4'-sulfophenyl)-3-methyl-5-pyrazolone.	Do.
85	do	2-methoxy-4-N-chloroformylmethyl-amino-6-fluoro-s-triazine.	1-(3'-sulfophenyl)-3-methyl-5-pyrazolone	Do.
86	do	2-phenoxy-4-N-chloroformylmethyl-amino-6-fluoro-s-triazine.	1-[5',7'-disulfonaphthyl-(2')]-3-methyl-5-pyrazolone.	Do.
87	do	2-ethoxy-4-N-chloroformylethylamino-6-fluoro-s-triazine.	1-[4',8'-disulfonaphthyl-(2')]-3-methyl-5-pyrazolone.	Do.
88	1,3-diaminobenzene-4-sulfonic acid	2-amylamino-4-N-chloroformylmethyl-amino-6-fluoro-s-triazine.	1-(4'-sulfophenyl)-5-pyrazolone-3-carboxylic acid.	Do.
89	do	2-dibutylamino-4-N-chloroformylmethyl-amino-6-fluoro-s-triazine.	1-(2'-fluoro-5'-sulfophenyl)-3-methyl-5-pyrazolone.	Do.
90	do	2-phenylamino-4-N-chloroformylmethyl-amino-6-fluoro-s-triazine.	1-chloroacetylamino-8-hydroxynaphthalene-3,6-disulfonic acid.	Red.
91	do	2-N-methyl-N-ethylamino-4-N-chloro-formylmethylamino-6-fluoro-s-triazine.	2-(β-bromopropionylamino)-8-hydroxy-naphthalene-3,6-disulfonic acid.	Scarlet.

EXAMPLE 92



42.1 parts of the sodium salt of the aminoazo dyestuff obtained by coupling of diazotized 2-aminonaphthalene-4,8-disulfonic acid with 1-amino-3-methylbenzene are dissolved in 400 parts of water and the solution is cooled to 0–5°. 24.2 parts of 2 - methylamino-4-N-chloroformyl-methylamino-6-fluoro-s-triazine dissolved in 100 parts of acetone are added dropwise to the solution within 30 minutes at this temperature and the pH of the reaction mixture is kept at 6.5–7.0 by the simultaneous addition

of sodium carbonate solution. As soon as no more free amino groups can be traced, a solution of 40 parts of a mixture of primary potassium phosphate and secondary sodium phosphate (weight ratio 1.8:1) in 200 parts of water is added to the reaction mixture. The new dyestuff is precipitated by the addition of sodium chloride, after stirring for 30 minutes it is filtered off and washed with dilute sodium chloride solution. The filter residue is mixed with 12 parts of a mixture of anhydrous primary potassium phosphate and anhydrous secondary sodium phosphate (ratio 1.8:1) and dried in vacuo at a temperature under 45°. After drying, the dyestuff is a yellow powder which dissolves in water with a yellow color.

4 parts of the new dyestuff are dissolved in 1000 parts of water and 20 parts of sodium carbonate are added. 100 parts of cotton are entered at 20° and the bath is heated to 40° within 30 minutes, 80 parts of sodium chloride are added to the solution and the goods are dyed for 1 hour at this temperature. The dyeing is then rinsed and soaped at the boil for 15 minutes. A deep yellow dyeing is obtained which has good fastness to water and light.

Other azo dyestuffs having similar properties are obtained by reacting the aminoazo dyestuffs given in the following Table 9 in the manner described in Example 92, with

(a) 2-methylamino-4-N-chloroformyl-methylamino-6-fluoro-s-triazine,

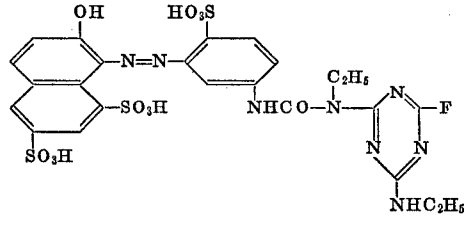
or with equivalent parts of

(b) 2-dimethylamino-4-N-chloroformyl-methylamino-6-fluoro-s-triazine,
(c) 2-ethylamino-4-N-chloroformyl-n-butylamino-6-fluoro-s-triazine, or
(d) 2-N-methyl-N-phenylamino-4-N-chloroformyl-methylamino-6-fluoro-s-triazine.

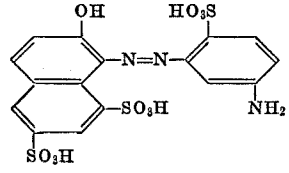
TABLE 9

Example No. (a–d)	Aminoazo dyestuff	Shade on cellulose fibres
93	2-aminonaphthalene-5,7-disulphonic acid → 1-aminobenzene.	Yellow.
94	2-aminonaphthalene-4,8-disulphonic acid → 1-amino-2-methoxy-5-methybenzene.	Do.
95	2-aminonaphthalene-6,8-disulphonic acid → 1-amino-3-methoxybenzene.	Do.
96	2-aminonaphthalene-4,8-disulphonic acid → 1-N-methylaminobenzene.	Do.
97	2-aminonaphthalene-4,6,8-trisulphonic acid → 1-aminobenzene.	Do.
98	2-aminonaphthalene-4,6,8-trisulphonic acid → 1-amino-3-methylbenzene → 1-aminobenzene.	Do.
99	4-aminoaxobenzene-3,4,'-disulphonic acid → 1-amino-3-methylbenzene.	Do.
100	2-aminonaphthalene-4,8-disulfonic acid → 1-aminonaphthalene-6-sulfonic acid → 1-methyl-3-aminobenzene.	Do.
101	1-aminobenzene-2,5-disulfonic acid → (3-aminophenyl)urea.	Do.

EXAMPLE 102



50.3 parts of the sodium salt of the aminoazo dyestuff of the formula



(obtained by coupling diazotised 2-amino-4-acetylaminobenzene sulphonic acid with 2-hydroxynaphthalene-6,8-disulphonic acid in an alkaline medium and saponifying the acetylamino group with sodium hydroxide solution) are dissolved with a neutral reaction in 800 parts of water. 26 parts of 2-ethylamino-4-N-chloroformyl-ethylamino-6-fluoro-s-triazine dissolved in 100 parts of acetone are added to this solution at 0–5°, the pH of the reaction solution being kept at 5–5.5 by the dropwise addition of sodium carbonate solution. When no more diazotisable amino groups can be traced, the dyestuff is completely precipitated by the addition of sodium chloride, isolated, stabilised with buffer salts and dried in vacuo at 40°. It dissolves easily in water with an orange color.

If cotton or staple fiber is printed by one of the usual methods with a printing paste consisting of 30 parts of this dyestuff, 200 parts of urea, 400 parts of water, 350 parts of 5%-aqueous sodium alginate solution and 20 parts of potassium carbonate, then dried, steamed for 10–15 minutes, then rinsed and finally soaped at the boil, an excellent wash-fast orange print is obtained.

By reacting equivalent amounts of the amino-azo dyestuffs listed in the following Table 10, in accordance with the procedures described in Example 102, with

(a) 26 parts of 2-ethyl-amino-4-N-chloroformyl-ethyl-amino-6-fluoro-s-triazine,

or with equivalent parts of

(b) 2-dimethylamino-4-N-chloroformyl-n-butylamino-6-fluoro-s-triazine,
(c) 2-N-methyl-N-phenylamino-4-N-chloroformyl-ethylamino-6-fluoro-s-triazine,
(d) 2-dimethylamino-4-N-chloroformyl-isopropyl-amino-6-fluoro-s-triazine,
(e) 2-(4'-chlorophenylamino)-4-N-chloroformyl-methylamino-6-fluoro-s-triazine,
(f) 2-(4'-methylphenylamino)-4-N-chloroformyl-methylamino-6-fluoro-s-triazine, or
(g) 2-N-methyl-N-(4'-methylphenylamino)-4-N-chloroformyl-methylamino-6-fluoro-s-triazine,

dyestuffs having similar properties, the shades on cellulose fibers of which are given in the following Table 10, are produced.

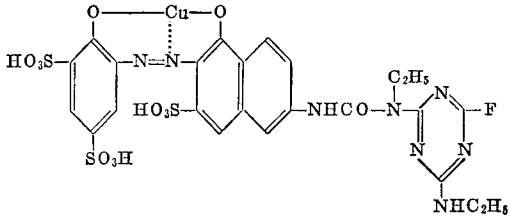
TABLE 10

Example No. (a–g)	Aminoazo dyestuff	Shade on cellulose fibres
103	2-amino-4-nitrobenzene sulphonic acid ——→ 1-benzoylamino-8-hydroxynaphthalene-4,6-di-sulphonic acid, reduced.	Red.
104	2-amino-4-nitrobenzene sulphonic acid ——→ 1-acetylamino-8-hydroxynaphthalene-3,6-di-sulphonic acid, reduced.	Red.
105	2-amino-4-nitrobenzene sulphonic acid ——→ 1-benzoylamino-8-hydroxynaphthalene-3,6-di-sulphonic acid, reduced.	Red.
106	2-amino-4-acetylaminobenzene sulphonic acid ——→ 1-hydroxynaphthalene-3,6-disulphonic acid, saponified.	Orange.
107	2-amino-4-acetylaminobenzene sulphonic acid ——→ 1-hydroxynaphthalene-4,6-disulphonic acid, saponified.	Red-orange.
108	1-aminobenzene-2,4-disulphonic acid alkaline ——→ 2-amino-5-hydroxynaphthalene-7-sulphonic acid.	Orange.
109	2-aminonaphthalene-1,5-disulphonic acid alkaline ——→ 2-methylamino-5-hydroxynaphthalene-7-sulphonic acid.	Reddish orange.
110	1-aminobenzene-2-sulphonic acid ——→ 1-(3'-aminobenzoylamino)-8-hydroxynaphthalene-3,6-disulphonic acid.	Red.
111	2-amino-4-acetylaminobenzene sulphonic acid ——→ 2-aminonaphthalene-5,7-disulphonic acid, saponified.	Orange.
112	2-amino-4-acetylaminobenzene sulphonic acid ——→ 1-(3'-sulphophenyl)-3-methyl-5-pyrazole imine, saponified.	Yellow.
113	1-amino-3-nitro-6-ethylbenzene ——→ 1-hydroxynaphthalene-3,6-disulfonic acid, reduced.	Reddish orange.
114	1-aminobenzene-3-N-methylsulfamide ——→ 1-amino-8-hydroxynaphthalene-3,6-disulfonic acid.	Red.
115	1-aminobenzene-3-N-(γ-hydroxypropyl)-N-methylsulfonamide ——→ 1-amino-8-hydroxynaphthalene-3,6-disulfonic acid.	Red.

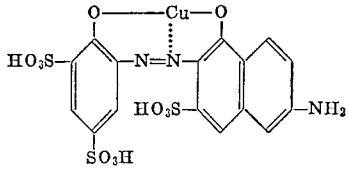
TABLE 10—Continued

Example No. (a-g)	Aminoazo dyestuff	Shade on cellulose fibres
116	4-amino-3-carboxy-benzene sulfonic acid ——→ 2-amino-5-hydroxy-7-sulfonic acid.	Orange.
117	1-aminobenzene-3-N-(β-hydroxyethyl)-N-methylsulfonamide ——→ 1-amino-8-hydroxynaphthalene-4,6-disulfonic acid.	Red.
118	3-amino-4-ethoxybenzene-sulfonic acid ——→ 2-amino-5-hydroxynaphthalene-7-sulfonic acid.	Orange.
119	1-aminobenzene-3-N-(β-sulfoethyl)-N-methylsulfonamide ——→ 1-amino-8-hydroxynaphthalene-3,6-disulfonic acid.	Red.
120	2-aminonaphthalene-4,6,8-trisulfonic acid ——→ 1-(4'-aminophenyl)-3-methyl-5-pyrazolone.	Yellow.
121	1-aminobenzene-3-N,N-bis-(γ-hydroxypropyl)-sulfonamide ——→ 1-amino-8-hydroxynaphthalene-3,6-disulfonic acid.	Red.
122	2,3'-diamino-diphenyl-1,1'-disulfimide ——→ 1-benzoyl-amino-8-hydroxynaphthalene-3,6-disulfonic acid.	Red.
123	2-aminonaphthalene-1,5,7-trisulfonic acid ——→ 2-amino-5-hydroxynaphthalene-7-sulfonic acid ——→ 1-amino-3-methylbenzene.	Red.

EXAMPLE 124



51.7 parts of the sodium salt of the copper-containing aminomonoazo dyestuff of the formula



(obtained by coupling diazotized 2-amino-1-hydroxybenzene-4,6-disulfonic acid with 2-amino-5-hydroxynaphthalene-7-sulfonic acid in an alkaline medium and treating the aminomonoazo dyestuff obtained with an agent giving off copper) are dissolved in 1000 parts of water. At 0–5°, a solution of 27.2 parts of 2-ethylamino-4-N-chloroformyl-ethylamino-6-fluoro-s-triazine in 100 parts of acetone is added and the pH of the reaction solution is kept at 5–5.6 by the addition of sodium carbonate solution. When no more free amino groups can be traced, the new dyestuff is completely precipitated by the addition of sodium chloride, buffer salts are added and the dyestuff is isolated and dried in vacuo at 40°. The dark powder dissolves in water with a ruby red color.

If cotton is padded with a 2%-solution of this dyestuff which also contains 2% of sodium bicarbonate, the impregnated goods are stored for 4 hours at room temperature, then soaped at the boil, and rinsed, a ruby red dyeing is obtained which has very good wet and light fastness properties.

Other metal-containing aminoazo dyestuffs are given in the following Table 11, which are reacted as described in Example 124 with

(a) 2-ethylamino-4-N-chloroformyl-ethylamino-6-fluoro-s-triazine,

or with equivalent amounts of

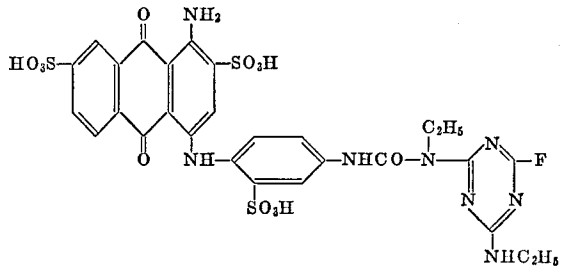
(b) 2-N-methyl-N-ethylamino-4-N-chloroformyl-ethylamino-6-fluoro-s-triazine, or

(c) 2-dimethylamino-4-N-chloroformyl-methyl-amino-6-fluoro-s-triazine.

TABLE 11

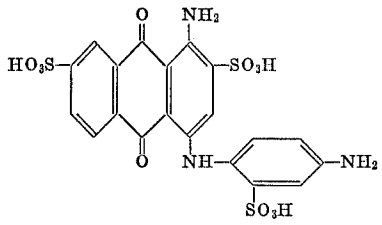
Example No. (a-c)	Metal-containing aminoazo dyestuffs	Shade on cellulose fibres
125	2-amino-1-hydroxybenzene-4-sulphonic acid alkaline ——→ 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid, copper complex.	Violet.
126	2-amino-1-hydroxybenzene-4-sulphonic acid alkaline ——→ 2-amino-8-hydroxynaphthalene-6-sulphonic acid, copper complex.	Bordeaux.
127	2-amino-1-hydroxybenzene-4,6-disulphonic acid alkaline ——→ 2-amino-5-hydroxynaphthalene-7-sulphonic acid, copper complex.	Ruby.
128	2-amino-1-hydroxybenzene-4-sulphonic acid alkaline ——→ 2-N-methylamino-5-hydroxynaphthalene-7-sulphonic acid, copper complex.	Do.
129	6-nitro-1-amino-2-hydroxynaphthalene-4-sulphonic acid alkaline ——→ 2-amino-5-hydroxynaphthalene-7-sulphonic acid, chromium complex 1:2.	Black.
130	4-nitro-2-amino-1-hydroxybenzene alkaline ——→ 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid, chromium complex 1:2.	Do.
131	4-nitro-2-amino-1-hydroxybenzene alkaline ——→ 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid, cobalt complex 1:2.	Black-brown.
132	2-amino-4-acetylamino-1-hydroxybenzene-6-sulphonic acid alkaline ——→ 1-amino-8-hydroxynaphthalene-2,4-disulphonic acid, copper complex, saponified.	Reddish navy blue.
133	2-amino-4-acetylamino-1-hydroxybenzene-6-sulphonic acid alkaline ——→ 1-phenylamino-8-hydroxynaphthalene-4,6-disulphonic acid, copper complex saponified.	Navy blue.
134	6-nitro-1-amino-2-hydroxynaphthalene-4-sulphonic acid alkaline ——→ 1-amino-8-hydroxynaphthalene-2,4-disulphonic acid, reduced, copper complex.	Blue.
135	2-amino-6-acetylamino-1-hydroxybenzene-4-sulphonic acid ——→ 1-hydroxynaphthalene-4,6-disulphonic acid, copper complex, saponified.	Ruby red.
136	2-amino-6-acetylamino-1-hydroxybenzene-4-sulphonic acid ——→ 1-(2',5'-disulphophenyl)-3-methyl-5-pyrazolone, copper complex, saponified.	Yellow brown.
137	1-hydroxy-2-amino-5-methylsulfonylbenzene ——→ 2-amino-8-hydroxynaphthalene-3,6-disulfonic acid, copper complex.	Ruby red.
138	3-amino-4-hydroxy-benzene sulfonic acid ——→ N-3'-aminophenyl acetyl acetic acid amide, cobalt complex 1:2.	Yellow.
139	3-hydroxy-4-amino-bromobenzene ——→ 1-amino-8-hydroxy-3,6-disulfonic acid, copper complex.	Violet.
140	1-hydroxy-2-aminobenzene-5-N-(β-methoxyethyl)-N-amylsulfonamide ——→ 2-amino-8-hydroxynaphthalene-3,6-disulfonic acid, copper complex.	Ruby red.

EXAMPLE 141



48.9 parts of 1 - amino-4-(4'-aminophenylamino)-anthraquinone-2,7-disulphonic acid are added at 20–25

in 500 parts of 30% oleum. The reaction mixture is stirred for 24–36 hours at 20–25°. The reaction mixture is then poured onto ice and the dyestuff which precipitates of the formula



is filtered off.

The filter cake, in the form of the sodium salt, is dissolved in 1000 parts of water. A solution of 26 parts of 2 - ethylamino - 4-N-chloroformyl-ethylamino-6-fluoro-s-triazine in 100 parts of acetone is added dropwise to this solution at 0–10° and the pH is kept at 5–5.5 by the simultaneous addition of sodium carbonate solution. On completion of the condensation, the new dyestuff is precipitated by the addition of sodium chloride, isolated, stabilized with buffer salts and dried in vacuo at 40°. It dissolves in water with a blue color.

If regenerated cellulose is padded with a 2%-solution of this dyestuff which also contains 10 g. of sodium bicarbonate and 50 g. of urea per liter, the impregnated goods are dried and heated for 2 minutes at 100–110°, then a pure blue dyeing is obtained which has very good fastness to washing and light.

Other aminoanthraquinone dyestuffs are given in the following Table 12 which are condensed as described in Example 141 with

(a) 2-ethylamino-4-N-chloroformyl-ethylamino-6-fluoro-s-triazine,

or with equivalent parts of

(b) 2-diethylamino-4-N-chloroformyl-methylamino-6-fluoro-s-triazine,

(c) 2-methylamino-4-N-chloroformyl-methylamino-6-fluoro-s-triazine,

(d) 2-N-methyl-N-(4'-chlorophenylamino)-4-N-chloroformyl-methylamino-6-fluoro-s-triazine,

(e) 2-N-methyl-N-(4'-ethoxyphenylamino)-4-N-chloroformyl-methylamino-6-fluoro-s-triazine,

or

(f) 2-phenylthio-4-N-chloroformyl-ethylamino-6-fluoro-s-triazines,

whereby reactive dyes of similar properties as those described in the preceding examples are obtained. Cellulose fibers dyed therewith have the shades given in the last column of Table 12.

TABLE 12

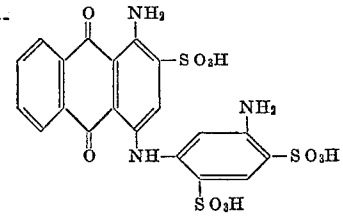
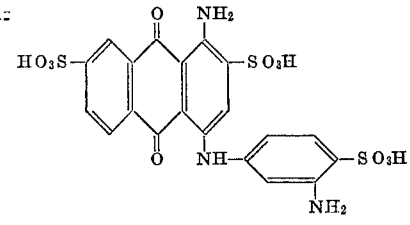
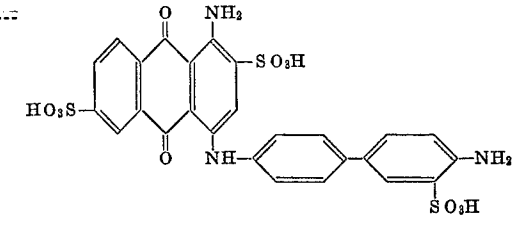
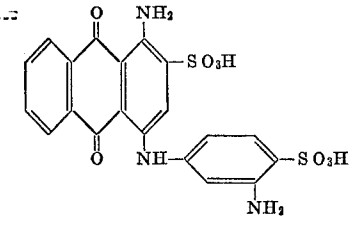
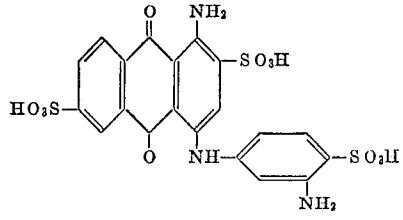
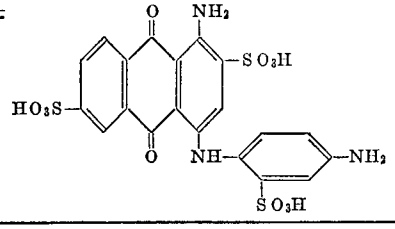
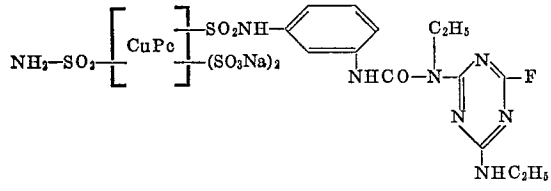
Example No. (a-f)	Aminoanthraquinone dyestuffs	Shade on cellulose fibres
142		Blue.
143		Do.
144		Do.
145		Do.

TABLE 12—Continued

Example No. (a-f)	Aminoanthraquinone dyestuffs	Shade on cellulose fibres
146		Blue.
147		Do.

EXAMPLE 148

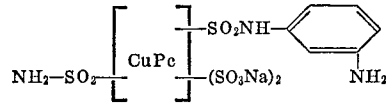


In this formula:

Pc represents the phthalocyanine structure.

57.6 parts of copper phthalocyanine are heated for 3 hours at 145° in 270 parts of chlorosulphonic acid. The solution is then cooled to 75° and 33.5 parts of thionyl chloride are added dropwise within 1 hour. The mixture is stirred for 3 hours at 70–75°, then cooled to room temperature and poured onto 1500 parts of ice. The suspension formed is filtered off and the precipitate is washed with 500 parts of 1% hydrochloric acid. The filter cake is then slurried in 500 parts of water and 300 parts of ice, stirred with 15 parts of m-aminoacetanilide and the pH is adjusted to 7 by the addition of aqueous ammonia solution. The temperature is then slowly allowed to rise to 40–50°, the pH of the suspension always being kept at 7.0–7.5 by the addition dropwise of ammonia solution. As soon as no more primary amine can be traced, 270 parts of 30% hydrochloric acid are added. The mixture is heated for 3 hours at 85–90° and in this way the acetylamino group is saponified.

The amino-phthalocyanine dyestuff of the formula



wherein Pc has the meaning given above, is so obtained.

This dyestuff is then isolated by filtration, again slurried in 1000 parts of water which is 0–5° cold and the pH of the suspension is adjusted to 8.0 with dilute sodium hydroxide solution. A solution of 26 parts of 2-ethylamino-4-N-chloroformyl - ethylamino - 6 - fluoro-s-triazine in 100 parts of acetone is poured into this suspension. Condensation is performed at 0–5° while stirring well and the hydrochloric acid liberated is neutralised by the addition dropwise of dilute sodium carbonate solution. On completion of the reaction, the new dyestuff is completely precipitated by the addition of sodium chloride, isolated in the presence of a buffering agent and dried in vacuo at 40°. It corresponds to the formula given at the beginning of this example.

If cotton is padded at 20° with a 2% solution of this dyestuff which also contains 20 parts of sodium bicarbonate and 200 parts of urea per litre, and the impregnated goods are dried, then heated for 4 minutes at 130–140° and finally soaped at the boil for 30 minutes, then a pure turquoise blue dyeing is obtained which has very good wet and light fastness properties.

Other amino-phthalocyanine dyestuffs are given in the following Table 13, which are condensed as described in Example 148 with

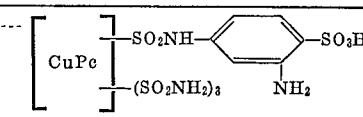
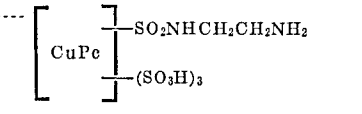
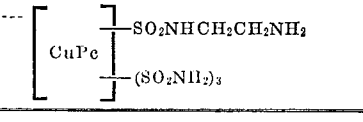
(a) 2-ethylamino - 4 - N - chloroformyl-ethylamino-6-fluoro-s-triazine,

or with equivalent parts of

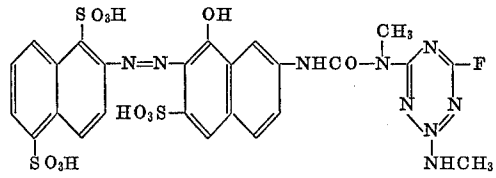
(b) 2-diethylamino-4 - N - chloroformyl - methylamino-6-fluoro-s-triazine,
(c) 2 - methylamino-4-N-chloroformyl - methylamino-6-fluoro-s-triazine,
(d) 2-(4'-methylphenylthio) - 4 - N - chloroformylmethylamino-6-fluoro-s-triazine,
(e) 2-morpholino - 4 - N - chloroformyl - methylamino-6-fluoro-s-triazine, or
(f) 2-piperidino - 4 - N - chloroformyl - propylamino-6-fluoro-s-triazine.

The resulting reactive dyes have similar good properties as those of the preceding examples, and dyeings produced therewith on cellulosic fibers, e.g. cotton, have the shades given in the last column of Table 13.

TABLE 13

Example No. (a-f)	Amino-phthalocyanine dyestuff	Shade on cellulose fibres
149		Turquoise blue.
150		Do.
151		Do.

EXAMPLE 152



23.9 parts of 2-amino-8-hydroxynaphthalene - 6 - sulphonic acid are dissolved in 400 parts of water, the pH being adjusted to 6.5 with sodium carbonate, and the solution is cooled to 0–5°. A solution of 24 parts of 2-methylamino-4-N-chloroformyl-methylamino - 6 - fluoro-s-triazine in 100 parts of acetate is added dropwise within 15 minutes at this temperature and the pH of the reaction mixture is kept at 4.5–5.5 by the addition of sodium carbonate solution. As soon as no more unchanged amino compound can be traced, 30 parts of sodium bicarbonate are added to the solution and then a solution of 30.3 parts of diazotised 2-aminonaphthalene - 1,5 - disulphonic acid is poured in. On completion of the coupling, sodium chloride and buffer salts are added to the reaction mixture, the precipitated dyestuff is filtered off, washed with sodium chloride solution and stabilised with buffer salts. After drying in vacuo at 40°, a red powder is obtained which dissolves in water with a red colour. If mercerised cotton is padded with a 2% solution of this dyestuff at 20°, dried and then treated with a 1% sodium hydroxide solution which also contains 30% sodium chloride, then steamed for 30 seconds at 100–103°, finally rinsed and soaped at the boil for 30 minutes, then a red dyeing is obtained which has very good wet and light fastness properties.

The following Table 14 lists the main moieties of other dyestuffs according to the invention having similar properties which are obtained by condensing the coupling components containing amino groups given in column III with

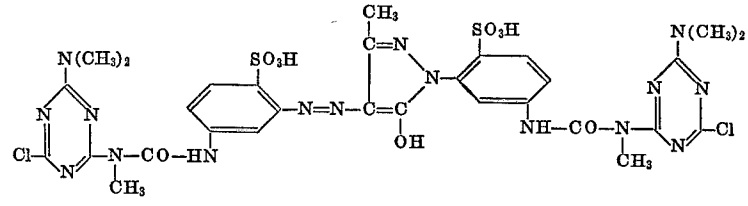
(a) 2 - methylamino-4-N-chloroformyl - methylamino-6-fluoro-s-triazine or equivalent parts of,
(b) diethylamino - 4 - N - chloroformyl-methylamino-6-fluoro-s-triazine,
(c) 2-(4'methoxyphenoxy) - 4 - N - chloroformyl-methylamino-6-fluoro-s-triazine, or
(d) 2-(4' - chlorophenoxy) - 4 - N - chloroformyl-ethylamino-6-fluoro-s-triazine,

as described in Example 152 and the condensation products are coupled as described in the same example, with the diazo components given in column II. The shades of dyeings with the resulting reaction dyes on cellulose fibers are given in column IV of Table 14.

TABLE 14

I	II	III	IV
Example No. (a–d)	Diazo component	Acylatable coupling component	Shade on cellulose fibres
153	1-aminobenzene-2-sulphonic acid	1-amino-8-hydroxynaphthalene-3,6-disulphonic acid	Red.
154	2-aminonaphthalene-1-sulphonic acid	do	Blueish red.
155	1-aminobenzene-2-sulphonic acid	1-amino-8-hydroxynaphthalene-4,6-disulphonic acid	Red.
156	2-aminonaphthalene-1,5-disulphonic acid	do	Blueish red.
157	1-aminobenzene-2,4-disulphonic acid	1-(4'-aminophenyl)-3-methyl-5-pyrazolone	Yellow.
158	1-aminobenzene-2,5-disulphonic acid	2-amino-5-hydroxynaphthalene-7-sulphonic acid	Orange.
159	1-aminobenzene-2-sulphonic acid	2-methylamino-5-hydroxynaphthalene-7-sulphonic acid	Do.
160	4-aminoazobenzene-3,4'-disulphonic acid	do	Scarlet.

EXAMPLE 161



18.8 parts of 1,3-diaminobenzene-4-sulphonic acid are dissolved in 400 parts of water at a pH-value of 4–4.5 and the solution is cooled to 0–5°. Then within 15 minutes 27 parts of 2-dimethylamino-4-N-chloroformyl - methylamino-6-chloro-s-triazine dissolved in 100 parts of acetone together with an aqueous solution of sodium carbonate are dropped into this solution in such a manner that the pH-value of the reaction mixture is maintained at 4–4.5. As soon as the reaction is completed, the reaction product is precipitated by addition of sodium chloride, filtered off, dissolved in 400 parts of water and diazotised at 0–5° with 25 parts of 30% hydrochloric acid and 6.9 parts of sodium nitrite. The resulting diazonium compound is coupled at a pH-value of 4–5 with a solution of 48 parts of the condensation product of 1-(2'-sulphonic acid-5'-aminophenyl) - 3 - methyl - 5 - pyrazolone and 2-dimethylamino - 4 - N - chloroformyl - methylamino-6-chloro-s-triazine (produced from the two components under the conditions described in Example 152). After completion of the coupling, the new dyestuff is precipitated with sodium chloride, filtered off and washed with diluted

sodium chloride solution. After drying in vacuo at 50°, a yellow powder is obtained which dissolves in water with a yellow colour.

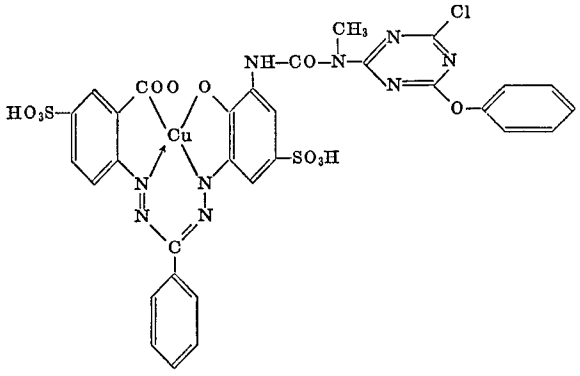
If cotton or staple fiber is dyed with the new dyestuff according to the application methods described in the preceding examples, a deep yellow dyeing of good fastness properties to light and wet is obtained.

Further dyestuffs with similar properties are obtained if the diazo and coupling components listed in the following Table 15 are reacted according to the conditions given in Example 161 with (a) 2-dimethylamino-4-N-chloroformyl - methylamino - 6 - chloro-s-triazine or equivalent parts of (b) 2-methylthio-4-N-chloroformyl - methylamino - 6 - chloro - s - triazine or (c) 2-dimethylamino-4 - N - chloroformyl - methylamino - 6 - fluoro-s-triazine and are then diazotized and coupled as described in the above example to form dyestuffs, the shade of which on cellulose fibers is given in the last column of the Table 15.

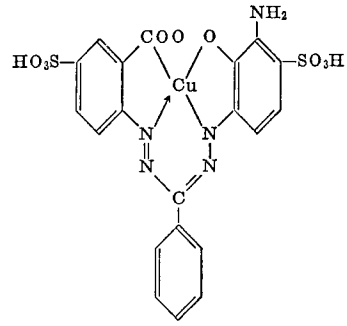
TABLE 15

Example No. (a–c)	Diazo component	Coupling component	Shade on cellulose fibres
162	1,3-diaminobenzene-4-sulphonic acid	1-amino-8-hydroxy-naphthalene-4,6-disulphonic acid	Red.
163	do	2-amino-8-hydroxy-naphthalene-6-sulphonic acid	Red.
164	do	2-ethylamino-8-hydroxy-naphthalene-6-sulphonic acid	Red.
165	do	1-(4'-aminophenyl)-5-pyrazolone-3-carboxylic acid	Yellow.
166	1,4-diaminobenzene-3-sulphonic acid	do	Do.

EXAMPLE 167



59.6 parts of the copper complex compound of the aminoformazane dyestuff of the formula



(obtained by coupling diazotized 6-acetylamino-2-amino-1-hydroxybenzene-4-sulphonic acid with the hydrazone from benzaldehyde and phenylhydrazine-2-carboxylic-acid-4-sulphonic acid reaction with a copper salt and saponification of the acetylamino group) are dissolved at a pH-value of 6–6.5 in 600 parts of water. 33 parts of 2-phenoxy-4-N-chloroformyl-methylamino - 6 - chloro-s-triazine dissolved in 80 parts of benzene together with an aqueous solution of sodium carbonate are dropped into this solution within one hour at 20–25° so that the reaction mixture remains neutral. As soon as no more starting material can be traced, the dyestuff is precipitated by addition of sodium chloride, filtered off, washed with diluted sodium chloride solution and dried cautiously in vacuo. It is a dark powder which, dissolved in warm water, gives a blue colour.

The 2 - phenoxy - 4 - N-chloroformyl-methylamino-6-chloro-s-triazine mentioned in the preceding example is obtained by known methods by reacting 1 mol of cyanuric chloride in a first step with 1 mol methylamine and in a second step with 1 mol phenol and finally treating the condensation product with phosgene in toluene.

By using equivalent amounts of the metal-containing aminoformazane compounds shown in columns II and III of the following Table 16 and the acylating agents listed in column IV, and by maintaining the reaction conditions described in the preceding Example 167, further dyestuffs according to the invention are obtained which have similar properties.

TABLE 16

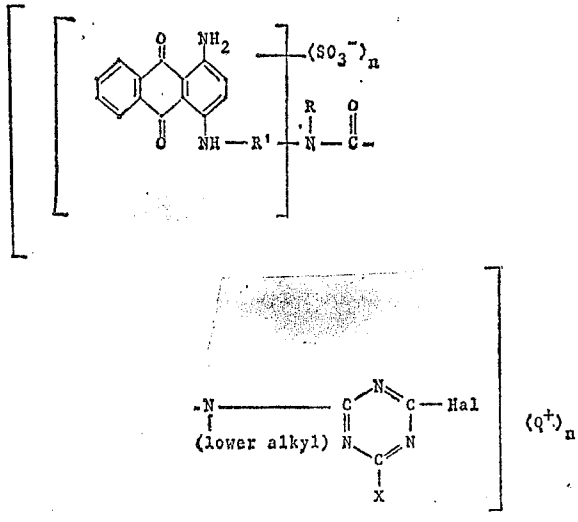
I	II	III	IV	V
Example No.	Aminoformazane dyestuff	Metal	Acylating agent	Shade on cellulose fibres
168	N-(2-hydroxy-3-aminophenyl-5-sulphonic acid)-N'-(2'-carboxy-phenyl-4'-sulphonic acid)-ms-phenylformazane.	Cu	2-dimethylamino-4-N-chloroformyl-methylamino-6-chloro-s-triazine.	Blue.
169	do	Cu	2-dimethylamino-4-N-chloroformyl-ethylamino-6-fluoro-s-triazine.	Do.
170	N-(2-hydroxy-3-aminophenyl-5-sulphonic acid)-N'-(2'-hydroxy-phenyl-3',5'-disulphonic acid)-ms-phenyl-formazane.	Cu	do	Do.
171	do	Cu	2-ethylthio-4-N-chloroformyl-ethylamino-6-chloro-s-triazine.	Do.
172	N-(2-hydroxy-3-aminophenyl-5-sulphonic acid)-N'-(2'-carboxyphenyl-4'-sulphonic acid)-ms-o-sulphonic acid phenyl-formazane.	Cu	2-dimethylamino-4-N-chloroformyl-methylamino-6-chloro-s-triazine.	Do.
173	do	Cu	2-dimethylamino-4-N-chloroformyl-methylamino-6-fluoro-s-triazine.	Do.
174	N-(2-hydroxy-3-aminophenyl-5-sulphonic acid)-N'-(2'-hydroxyphenyl-3',5'-disulphonic acid)-ms-o-sulphonic acid phenyl-formazane.	Cu	do	Do.
175	do	Cu	2-dimethylamino-4-N-chloroformyl-methylamino-6-chloro-s-triazine.	Do.
176	do	Cu	2-phenylthio-4-N-chloroformyl-methylamino-6-chloro-s-triazine.	Do.

EXAMPLE 177

100 parts of wool are introduced into a liquor consisting of 4000 parts of water of 40°, 2 parts of the dyestuff according to Example 1, 5 parts of 30% acetic acid and 0.5 part of a condensation product of stearyl amine and ethylene oxide. Within 20 minutes, the temperature of the dye bath is increased to boiling and maintained at the boil for one hour. After rinsing and drying, a brilliant yellow wool dyeing is obtained which has good wet and light fastness properties.

We claim:

1. An anthraquinone dyestuff of the formula



wherein

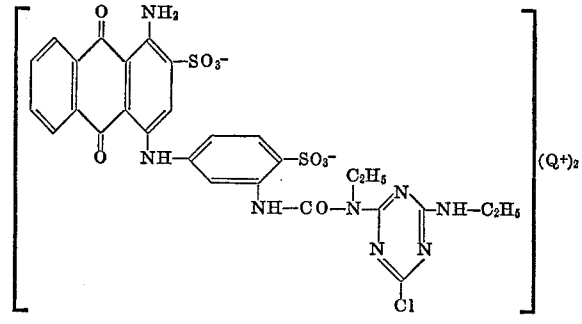
R′ is phenylene or diphenylene,
n is 2 or 3,
Q^+ is hydrogen ion, ammonium ion, or sodium or potassium metal ion,
R is hydrogen or lower alkyl,
Hal is F, Cl or Br, and
X is a monovalent electron-donor substituent,

selected from the group of lower alkoxy, phenoxy, halogen-substituted phenoxy, lower alkyl-substituted

phenoxy, lower alkoxy-substituted phenoxy, lower alkythio, phenylthio, halogen-substituted phenylthio, lower alkyl-substituted phenylthio, lower alkoxy-substituted phenylthio, lower alkylamino, di(lower)-alkylamino, phenylamino, N-lower alkyl-N-phenylamino, N-lower alkyl-N-halogenphenylamino, N-lower alkyl-N-lower alkylphenylamino, N-lower alkyl-N-lower alkoxyphenylamino, piperidino or morpholino, halogen being chloro or bromo.

2. An anthraquinone dyestuff according to claim 1 wherein X is a dialkylamino radical, each alkyl moiety of said radical having up to four carbon atoms.

3. An anthraquinone dyestuff according to claim 1 of the formula



wherein

Q^+ represents hydrogen ion, ammonium ion or sodium or potassium metal ion.

References Cited

UNITED STATES PATENTS

3,110,710 11/1963 Rattee et al. ------ 260—249 XR

JOHN M. FORD, Primary Examiner

U.S. Cl. X.R.

260—247.2 A, 249.5, 146 T, 153, 242; 8—39, 42 B, 163